

Isolable *p*- and *m*-[(^tBu₂MeSi)₂Si]₂C₆H₄: Disilaquinodimethane vs Triplet Bis(silyl radical)

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Supporting Information

ABSTRACT: Isomeric *p*- and *m*-disilaquinodimethanes 2 and 4 were synthesized by the reductive dehalogenation of the corresponding *p*- and *m*-bis(halosilyl)benzenes 1 and 3, respectively, and were isolated and structurally characterized. The X-ray diffraction and solid-state NMR studies of 2 revealed its singlet quinodimethane structure featuring two exocyclic Si≡C double bonds with some singlet biradical contribution. In contrast, the X-ray crystallography and EPR measurements of 4 disclosed its biradical nature, described as a triplet ground state bis(silyl radical).

Organic free radicals are open-shell species featuring an unpaired electron and are ubiquitous in a variety of chemical transformations. To date, a number of free radicals have been classified as persistent or even isolable species, in which the highly reactive odd-electron centers are stabilized by either thermodynamic or kinetic means.¹ On the other hand, the high-spin molecules possessing several radical centers in a single molecule and serving as model compounds for the design of organic ferromagnetic materials^{1,2} are more challenging, especially from the viewpoint of potential communication between the radical centers. Among the most representative examples of such species, one can mention *p*- and *m*-quinodimethane derivatives, of which the *para*-isomer is known to possess a singlet ground state with a closed-shell quinoid form,³ whereas the *meta*isomer was shown to manifest a robust triplet ground state.⁴

The heavy analogues of organic free radicals featuring an unpaired electron on a silicon, germanium, tin, or lead atom as the key reactive intermediates in a number of organometallic transformations represent another important synthetic challenge.⁵ Although the first persistent radicals of the type $[(Me_3Si)_2$ - $CH]_{3}E^{\bullet}$ (E = Si, Ge, Sn) were reported by Lappert and coworkers as early as 1973,⁶ the isolation and structural characterization of the first stable cyclotrigermenyl radical was reported by Power et al. in 1997,^{7a} and then the stable silyl radical was achieved in 2001 with the synthesis of a cyclotetrasilenyl radical.^{7b} Since then, several other representatives of isolable silyl,⁸ germyl,^{8,9} stannyl,¹⁰ and plumbyl¹¹ radicals have been reported, including neutral acyclic nonconjugated radicals, cyclic radicals, and charged radical species (such as silvlene anion-radical, disilene anion-radical and cation-radical, and disilyne anion-radical) as well as singlet biradicaloid species.¹² However, despite such recent advances in the field, oligo-radicals with two (or more) heavy group 14 element radical centers have remained elusive.

In this paper, we report the synthesis and structural identification of the isomeric *p*- and *m*-disilaquinodimethanes **2** and **4**, of which the former is classified as having a predominantly singlet ground-state *p*-disilaquinodimethane form featuring two exocyclic Si=C bonds, whereas the latter was found to represent a triplet ground-state bis(silyl radical).

1,4-Bis(bromosilyl)benzene derivative 1 was reduced with 2 equiv of KC₈ in dry THF at -78 °C, forming 3,6-bis[bis(di-*tert*butylmethylsilyl)silylidene]cyclohexa-1,4-diene (2), which was isolated from pentane as air-sensitive purple crystals in 23% yield (Scheme 1). Likewise, the meta-isomer, 1,3-bis[bis(di-tert-butylmethylsilyl)silyl]benzene-1',1"-diyl (4), was prepared by reduction of the corresponding precursor, 1,3-bis(iodosilyl)benzene derivative 3, and isolated by recrystallization from pentane as airsensitive yellow crystals in 29% yield (Scheme 1).^{13,14} The electronic spectra of isomeric 2 and 4 were distinctly different (see the Supporting Information). Thus, the longest wavelength absorption of 2 was remarkably red-shifted compared with that of 4 (2, 555 nm (ε 6800) vs 4, 414 nm (ε 870), 433 nm (ε 780)),¹⁴ pointing to different electronic structures for 2 and 4. Such a distinction was demonstrated by X-ray crystallographic studies, which revealed that in their crystalline form these two isomers have quite different geometries. Thus, 2 exhibited a disilaquinodimethane structure with trigonal-planar configuration at the Si1 and Si1[#] atoms (sum of the bond angles 359.96°) and coplanar alignment of the 3p(Si) and 2p(C) (aromatic ring) orbitals, allowing their effective π -conjugation (Figure 1, left).¹⁴ The Si1-C1 bond of 1.8174(14) Å is notably shorter than typical Si-C(aryl) single bonds (1.879 Å),¹⁵ although longer than the Si=C bonds in previously reported silenes (1.702-1.775 Å).¹⁶ Within the six-membered ring, C–C bond alternation characteristic of the cyclohexa-1,4-diene system was observed, C1-C2 =1.423(2) Å, $C1-C3^{\#} = 1.422(2)$ Å, C2-C3 = 1.3700(19) Å, although the extent of such alternation ($\Delta \approx 0.05$ Å) was smaller than that of the carbon analogue, tetraphenylparaquinodimethane $(\Delta = 0.10 \text{ Å})$.^{3b} These structural features of 2 imply that its structure is best described as the predominant contribution of the closed-shell quinoid form with some (but by no means full) contribution of the singlet bis(silyl radical) character. The solid-state ¹³C and ²⁹Si NMR spectra of 2 are also in accord with its formulation as the pdisilaguinodimethane derivative: the resonances observed at 156.3 ppm (¹³C NMR) and 91.1 ppm (²⁹Si NMR) are typical for the doubly bonded C and Si atoms of stable silenes Si=C.

In contrast, in 4 the 3p(Si) and 2p(C) (aromatic ring) orbitals are orthogonal to each other, an arrangement that prevents their

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Scheme 1. Synthesis of the Disilaquinodimethane 2 and Bis(silyl radical) 4





the tert-butyl groups on Si3 is disordered, and the minor contribution (occupancy factor 0.299) and hydrogen atoms are omitted for clarity. # indicates the following symmetry transformation: $-x_1 - y + 1$, $-z_2$. Selected bond lengths (Å) and angles (deg): Si1-Si2 = 2.3675(6), Si1-Si3 = 2.3737(6), Si1-C1 = 1.8174(14), C1-C2 = 1.423(2), $C1-C3^{\#} = 1.422(2), C2-C3 = 1.3700(19). Si2-Si1-Si3 = 122.86(2),$ Si2-Si1-C1 = 117.52(5), Si3-Si1-C1 = 119.58(5), Si1-C1-C2 = 120.66(11), $Si1-C1-C3^{\#} = 124.39(11)$, $C2-C1-C3^{\#} = 114.94(12)$, $C1-C2-C3 = 122.78(13), C2-C3-C1^{\#} = 122.29(13).$ (Right) ORTEP drawing of 4 (50% probability level). Hydrogen atoms are omitted for clarity. # indicates the following symmetry transformation: -x + 1/2, -y + 1/2, z. Selected bond lengths (Å) and angles (deg): Si1-Si2 = 2.3554(14), Si1-Si3 = 2.3524(14), Si1-C2 = 1.9108(19), $C1-C2 = 1.387(3), C1-C2^{\#} = 1.387(3), C2-C3 = 1.395(5),$ $C3-C4 = 1.386(4), C4-C3^{*} = 1.386(4). Si2-Si1-Si3 = 122.21(5),$ Si2-Si1-C2 = 117.15(5), Si3-Si1-C2 = 119.29(5), $C2-C1-C2^{\#} =$ 123.2(4), Si1-C2-C1 = 120.8(3), Si1-C2-C3 = 121.73(17), $C1-C2-C3 = 117.5(2), C2-C3-C4 = 121.0(3), C3-C4-C3^{\#} =$ 119.7(4).

 π -bonding, although the geometry at both Si1 and Si1[#] atoms is still nearly trigonal-planar (sum of the bond angles 358.65°) (Figure 1, right).¹⁴ Accordingly, the Si1-C2 and Si1[#]-C2[#] bonds of 1.9108(19) Å were no longer shortened, and C-C bond alternation was not observed within the six-membered ring, pointing to its 6π -electron aromaticity. Such structural peculiarities of 4 permit its classification as a bis(silyl radical) bridged by a *m*-phenylene group, and indeed computations showed the preference for the triplet ground state of 4 over its singlet state by ${\sim}20\,\mathrm{kcal/mol.^{17}}$ Such an assumption on the spin multiplicity of 4 was further corroborated by its EPR measurements. The EPR spectrum of 4 (Figure 2) measured at 80 K in 3-methylpentane showed characteristic signals at 335.2 mT (g = 2.0034). As is well known, the EPR resonances of triplet biradicals are split by the magnetic dipole-dipole interaction between unpaired electrons (zero-field splitting, ZFS).¹⁹ Accordingly, the EPR signal of 4 was split into six lines with the ZFS parameters $D = 6.4 \times 10^{-3} \text{ cm}^{-1}$ (13.8 mT) and $E = 0.80 \times 10^{-3} \text{ cm}^{-1}$ (1.72 mT). The average distance between the unpaired electrons in 4 was thus estimated as 5.89 Å, assuming the point-dipole approximation, a value that is close to the distance of 5.72 Å determined from the X-ray



Figure 2. EPR spectrum of **4** in 3-methylpentane at 80 K. The peaks marked by \times are due to a monosilyl radical impurity.

Scheme 2. Reactivity of the Disilaquinodimethane 2 and Bis(silyl radical) 4



crystal structure, indicating that in 4 the two unpaired electrons reside mainly on the silicon atoms. A resonance at 167.4 mT was observed in a characteristic half-field region corresponding to a forbidden $\Delta m = 2$ transition. The temperature-dependent EPR measurements of this signal intensity revealed that it follows the Curie law (see the Supporting Information),¹⁸ indicating that 4 represents a triplet ground-state biradical, despite the perpendicular arrangement of its *m*-phenylene π -orbitals and 3p(Si) orbitals holding unpaired electrons, in contrast to the coplanar conjugated system of these orbitals in the carbon analogue.^{1,2}

In accord with their differing structures, **2** and **4** react differently with MeOH and 1,4-cyclohexadiene (Scheme 2). Thus, **2** is reactive toward both MeOH (as a typical reagent for silenes) to give the 1,6-adduct **5** and 1,4-cyclohexadiene (as a hydrogen donor) to give the hydrogen-abstraction product **6** in quantitative yields.¹⁴ These results indicate that **2** has both a Si=C double bond and bis(silyl radical) reactivity. On the other hand, although **4** failed to react with MeOH, it quantitatively reacted with 1,4-cyclohexadiene to form *m*-bis(hydrosilyl)benzene 7,¹⁴ indicating that **4** has only bis(silyl radical) reactivity.

In summary, we have succeeded in the synthesis, isolation, and structural characterization of the first stable p- and m-disilaquinodimethane derivatives, **2** and **4**. Their noticeable differences are the alignments of the 3p(Si) and 2p(C) (aromatic ring) orbitals. The former exhibited a nearly planar arrangement, giving a p-disilaquinodimethane structure, whereas the latter exhibited an orthogonal arrangement, leading to a diradical structure with a triplet ground state.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectral data for compounds 1–7; tables of crystallographic data, including atomic positional and thermal parameters, and CIF files for 2 and 4; UV–vis spectral charts of 2 and 4; temperaturedependent EPR spectral chart of 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Reduction of the corresponding 1,3-bis(bromosilyl)benzene derivative with potassium graphite in THF failed to produce the desired **4**.

(14) For the synthesis as well as spectral and crystal data of new compounds 1-7, see the Supporting Information.

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(18) For temperature-dependent EPR measurements of 4, see the Supporting Information.

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